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NATIONAL WATER RESEARCH INSTITUTE

INSTITUT NATIONAL de RECHERCHE sur les EAUX

Environment Canada Environnement

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RESEARCH AND APPLICATIONS BRANCH

ANNUAL REPORT

1991-92

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National Water Research Institute
Burlington, Ontario L7R 4A6

July 1992

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List of Acronyms

AAS	Atomic Absorption Spectrophotometry
AED	Atomic Emission Detector
AES	Atmospheric Environment Service
AVS	Acid Volatile Sulfide
CAEAL	Canadian Association of Environmental Analytical Laboratories
CAPCO	Canadian Association of Pesticide Control Officials
CB	Chlorobenzene
CCIW	Canada Centre for Inland Waters
CE	Capillary Electrophoresis
CEPA	Canadian Environmental Protection Act
CHCL	Clean and Hazardous Chemicals Laboratory
CRM	Certified Reference Material
DCDF	Polychlorinated Dibenzofuran
DFO	Fisheries and Oceans Canada
DNA	Desoxyribonucleic Acid
DOE	Environment Canada
ECD	Electron Capture Detector
EIA	Enzyme Immunoassay
EP	Environmental Protection
EPA	Environmental Protection Agency
ESED	Ecosystem Sciences and Evaluation Directorate
F&HM	Fisheries and Habitat Management
FIA	Flow Injection Analysis
FY	Fiscal Year
GC	Gas Chromatography
GLLFAS	Great Lakes Laboratory for Fisheries and Aquatic Sciences
GLSE	Goulden Large-Sample Extractor
GLWQA	Great Lakes Water Quality Agreement
GPC	Gel Permeation Chromatography
IA	Immunoassay
ICP	Inductively Coupled Plasma
ISP	Ion-Spray
LC	Liquid Chromatography
LEAFS	Laser Excited Atomic Fluorescence Spectrophotometry
LRB	Lakes Research Branch
MAB	Monoclonal Antibodies
MS	Mass Spectrometry

List of acronyms (continued)

NDBC	National Data Buoy Center
NLET	National Laboratory for Environmental Testing
NPD	Nitrogen Phosphorus Detector
NRC	National Research Council
NWRI	National Water Research Institute
OCS	Octachlorostyrene
OPA	o-phthalaldehyde
OR	Ontario Region
PAH	Polynuclear Aromatic Hydrocarbon
PCB	Polychlorinated Biphenyl
PCDD	Polychlorinated Dibenzo-*p*-dioxin
PERD	Interdepartmental Panel on Energy Research and Development
QA	Quality Assurance
QC	Quality Control
RAB	Research and Applications Branch
R&D	Research and Development
RIA	Radioimmunoassay
RM	Reference Material
RRB	Rivers Research Branch
SFE	Supercritical Fluid Extraction
SISB	Surveys and Information Systems Branch
SWADE	Surface Wave Dynamics Experiment
TCDD	Tetrachlorodibenzo-*p*-dioxin
TCDF	Tetrachlorodibenzofuran
TKN	Total Kjeldahl Nitrogen
USGS	U.S. Geological Survey
WAVES	Water-Air Vertical Exchange Study
WNR	Western and Northern Region
WPMB	Water Planning & Management Branch
WQB	Water Quality Branch

Preamble

It is my pleasure to present to our clients, collaborators and colleagues this annual report covering the activities of the Research and Applications Branch, National Water Research Institute, for the period April 1, 1991 to March 31, 1992.

In keeping with current austerity measures in the Department, this year's report is somewhat shorter than in the past but we have tried to ensure that it captures the key findings of our research programme.

Requests for additional information or comments related to material in this report should be directed to the appropriate study leader or to the Branch Director's Office.

John Lawrence
Director

ANALYTICAL CHEMISTRY RESEARCH

STUDY NO.: **84009**

STUDY TITLE: **Electrokinetic Detection of Toxic Effects**

STUDY LEADER AND TEAM: **S.A. Daniels**

INTRODUCTION: Toxicity in its most serious forms are commonly characterized by changes in the genetic coding responsible for protein replication. Such coding is embodied in the nucleic acid moiety of the cell. Mis-coding is frequently evidenced as mutagenicity when changes occur within the nucleic acids themselves. This phenomenon is considered to be one of the most detrimental effects of environmental contamination; and as such, appropriate techniques are required for its ready detection and characterization.

The ability to make such determinations in a quick and cost-effective manner, would be of great utility to monitoring agencies and environmental analytical laboratories such as the NLET where interest in this application had its origin. Another advantage is the savings in time and resources by having the capability to screen-out toxicologically benign samples which would otherwise require extensive analytical attention. Private-sector groups would also benefit greatly from methods which not only identify mutagenicity but also serve to characterize the problem. The target for the study year involves the development of electrophoretic methods suitable for the detection of genetic damage due to environmental contaminants.

RESULTS: The process has been completed which evaluated the ion-spray mass spectrometer (ISP-MS) for the detection of DNA adducts. The ISP-MS showed excellent sensitivity to a number of nucleotides, nucleosides, and synthetic adducts of DNA. These were achieved using liquid chromatography (LC)/MS, LC/UV, MS/MS, and MS/MS/MS. The development of a capillary electrophoresis (CE)/MS interface took considerably more time than had been envisaged; and as a result, the time strictures of this phase of the study precluded the examination of DNA adducts by this technique. A complete evaluation of the ISP-MS involving quantitative elements was also precluded by an excessive workload at NRC which rendered the instrumentation unavailable.

Procedures for DNA fragment separation and recognition by gel electrophoresis was improved upon by examination of ligated reference DNA as well as DNA extracted from fish tissue.

PUBLICATIONS:

Daniels, S.A. and S.S. Rao. 1992. Response of Aquatic Bacterial Agregates to an Environmental Contaminant. NWRI Contribution No. 92-09.

Daniels, S.A., M. Quilliam and R.K. Boyd. 1992. Evaluation of Ion-Spray Mass Spectrometry for the Detection of DNA Adducts. NWRI Contribution No. 92- .

STUDY NO.: **84010**

STUDY TITLE: **Multi-dimensional Instrumental Techniques for Trace Analysis**

STUDY LEADER AND TEAM: **B.K. Afghan, D. Barclay and R.J. Wilkinson**

INTRODUCTION: Multi-dimensional techniques, based on Column Liquid Chromatography, are very promising techniques for the determination of 80-90% of the organic compounds currently not determinable by GC or GC/MS. The purpose of this study is to develop appropriate methods for those contaminants which are difficult to analyze by classical GC and GC/MS technology. Our efforts are devoted to analyze semi-volatile and non-volatile analytes of environmental significance. Target analytes include chlorinated polar compounds from the pulp and paper industry, nitro-PAHs, hetrocyclics and hydroxy/COOH/NH_2 containing organic contaminants.

RESULTS: Four systems were configured consisting of single column/multi-detector systems and multi-column/multi-detector systems. A post-column derivatization module was also assembled to interface with the above systems.

A multi-detector system employing photo-diode-array/fluorescence/photo-conductivity/ chemiluminescence detectors has been evaluated in the FIA mode for the identification and confirmation of PAHs, nitro-PAHs and carbamates. The system shows promise as a quantitative and confirmatory tool for the above classes of compound.

The post-column derivatization system was tested on carbamates. Post column on-line hydrolysis and derivatization was carried out using MgO and OPA. It was found that fine particles of MgO blocked the flow and damaged the mixing coils and the flow cell of the detector. Attempts to segregate fine particles by decantation and/or mixing with silica prior to packing the column were not successful. The use of coarse particles of MgO or strong anion exchangers such as Amenix will be evaluated in the future.

A multi-column/multi-detector LC system utilizing GPC/Si/normal phase/reverse phase columns has been developed. The system is capable of operating with up to 6 different columns and 5 detectors simultaneously. It is possible to back flush certain columns and to operate in any configuration necessary to meet the separation requirements of the analysis. Initially, the system will be used to fractionate complex environmental samples by size of molecules and polarity.

Micro-LC has been interfaced with an electron capture detector (ECD). The system will be evaluated using normal phase for the determination of organochlorine pesticides and PCBs. Attempts will also be made to determine chlorinated phenols using the micro-LC/ECD system.

STUDY NO.: **84011**

STUDY TITLE: **Separation and Extraction Techniques: Electrokinetic Chromatography of Polyaromatic Hydrocarbons**

STUDY LEADER AND TEAM: **F.I. Onuska and K.A. Terry**

INTRODUCTION: This study continues to be focussed on the investigation of the following separation and extraction techniques: (i) High-voltage electrophoresis performed in open tubular capillary columns for the electrokinetic separation of neutral molecules in aqueous micellar solutions; (ii) A microwave extraction system for the extract of solid and aqueous matrices; and (iii) Supercritical fluid extraction of fly ash samples.

RESULTS: An electrophoretic method was devised for the separation of polyaromatic hydrocarbons (PAHs). The electrophoretic buffer used in these experiments consisted of tetrahexylammonium perchlorate dissolved in acetonitrile modified with varying amounts of water. When analyte molecules are dissolved in this buffer, they undergo solvophobic interaction with tetrahexylammonium ions, forming a positively charged species that can migrate in an electric field. Baseline separations for 1-methyl pyrene (100 ng/μL), anthracene (100 ng/μL) and naphthalene (500 ng/μL) were successfully obtained using this method. The elution order indicated that the larger molecules are more tightly bound to the tetrahexylammonium moiety than the smaller or more polar solutes such as naphthalene. Further experiments will be carried out to investigate separation possibilities of PAHs employing the inclusive complexation properties of cyclodextrins.

Microwave extraction activities were focussed on the heat and mass transfer of analytes from a dielectric to a nonmiscible organic solvent. The interior electric field, the moisture movement in solid porous materials and the continuous changes in the dielectric and other properties combine to make microwave extraction processes every complex. This novel extraction technique was found to reduce extraction times for PCBs and organochlorine pesticides by at least 80% compared to Soxhlet extraction or liquid-liquid extraction. The yields of the extracted analytes obtained using the microwave technique were compared with those obtained by the Soxhlet method. Similar comparisons were made between convectional heat and electromagnetic waves for extraction purposes. Due to the considerable savings in time and energy, this novel method is ideal for fast extractions of large number of samples.

Supercritical fluid extraction of fly ash samples was carried out. The recoveries obtained for polychlorinated dibenzo-p-dioxins and dibenzofurans showed that nitrous oxide plus methanol or toluene provide higher yields than 24-hour Soxhlet extractions with toluene.

PUBLICATIONS:

Onuska, F.I. and S. Davis. 1991. Multivariate Observations of the PCBs in Environmental Compartments of Two Harbours. J. Environ. Anal. Chem. 43: 137-150.

Onuska, F.I. and K.A. Terry. 1991. Supercritical Fluid Extraction of Polychlorinated Dibenzo-p-Dioxins from Municipal Incineration Fly Ash. J. High Resolut. Chromatogr. 14: 829-834.

Onuska, F.I. and K.A. Terry. 1991. Preliminary Examination of the Photoionization Detector for Microbore Column Supercritical Fluid Chromatography. J. Microcol. Sep. 3: 33-37.

Onuska, F.I. and K.A. Terry. 1992. Micellar Electrokinetic Chromatography: UV-longitudinal Flow Cell Design with Enhanced Sensitivity for Environmental Analysis. NWRI Contribution No. 92-07.

Onuska, F.I. 1992. Contribution to Organic Trace Analysis of Micropollutants in the Great Lakes Basin. D.Sc. Thesis, Charles University, Prague, Czechoslovakia.

STUDY NO.: **84012**

STUDY TITLE: **Preconcentration For Ultratrace Analysis**

STUDY LEADER AND TEAM: **D.H.J. Anthony and I. Sekerka**

INTRODUCTION: The overall purpose of this study is to provide the Department with the capability to measure "culprit" toxic organic contaminants in water (e.g. CEPA Priority Substances, Niagara River and Lake Ontario Toxics Management Plans substances) at their ambient, generally ultratrace, levels. Research and development conducted in this study to date was focussed on immiscible solvent extraction as the fundamental preconcentration technique and has produced a continuous-flow solvent extraction technology (the Goulden Large-Sample Extractor (GLSE)) which has proved useful for these purposes by several agencies responsible for water quality monitoring and research (e.g. Environment Canada, US EPA, USGS). The major objective of this study for FY 91/92 was to improve this technology, making it more effective for field and laboratory applications, particularly with respect to analytical recovery of dissolved solvent. A second objective of the study was to begin research into the development of alternative preconcentration techniques requiring minimum use of organic solvents.

RESULTS: A GLSE prototype possessing an efficient analytical solvent recovery process has been developed and undergone preliminary laboratory and field testing. The prototype design also minimizes exposure of operating staff to solvent vapours and entrainment of airborne contaminants in the extraction apparatus. Replicas of the prototype have been manufactured by the private sector for use by the WQB/OR in monitoring Great Lakes Connecting Channels water quality (e.g. Niagara River).

Preliminary work in the design of a sampling system to effectively compare solvent extraction and solid-phase extraction in preconcentration of organic contaminants from large samples has been completed.

PUBLICATIONS:

Merriman, J.C., D.H.J. Anthony, J.A. Kraft, and R.J. Wilkinson. 1991. Rainy River Water Quality in the Vicinity of Bleached Kraft Mills. Chemosphere 23 (11/12): 1605-1615.

PRESENTATIONS:

Anthony, D.H.J. "Preconcentration for Ultratrace Determination of Organic Contaminants in Aqueous Matrices using a Continuous-Flow Solvent Extraction Technique". Presented at the 74th Chemical Conference and Exhibition, Hamilton, Ontario, June 02-06, 1991.

TECHNOLOGY TRANSFER:

Trained and assisted staff of the WQB/WNR in the incorporation of GLSE technology in their water quality monitoring applications (Saskatoon, May 27 - June 01, 1991; Regina, October 15 - 25, 1991).

STUDY NO.: **84013**

STUDY TITLE: **Automated Analytical Systems**

STUDY LEADER AND TEAM: **I. Sekerka, J. Lechner and D.H.J. Anthony**

INTRODUCTION: The R&D work carried out under this study is focussed on developing analytical methods for water quality assessment and monitoring as required by CEPA and GLWQA programs. The improvement of the effectiveness and economy of environmental laboratories is another goal of the study. The following objectives have been established for 1991-92: (i) Optimize the Microwave digestion for determination of heavy metals; (ii) investigate the use of a supercritical water system for sample digestion; (iii) develop a method for the determination of Acid Volatile Sulfide (AVS) in sediments.

RESULTS: The success achieved with the design, construction and performance of the Laser Excited Atomic Fluorescence Spectrophotometer (LEAFS) made the investigation and development of sample digesting systems of secondary importance. A LEAFS method for the direct determination of lead down to 0.4 ppt was developed that does not require any preconcentration and/or pretreatment steps. This is the first time that direct analysis at such low concentrations has been accomplished. (See Study 84019).

The content of AVS is a very important factor influencing the toxicity of sediments. At the request of A. Mudroch, Lakes Research Branch, a reliable, simple, efficient and cost effective method for the determination of AVS has been developed. It is based on the conversion of the solid and ionic sulfides of the sediment sample to the gaseous form at pH << 1. The gas diffuses through the wall of gas-permeable tubing into the stream of sodium hydroxide solution. The resulting ionic form of sulfide is then monitored either by ion selective electrode or amperometrically in a flow-through cell of the detector. The square area of registered peaks corresponds to the concentration of AVS in the sample. A detection limit of 1.0 ppb with a relative standard deviation of 5% has been achieved using an 0.5 g sample. The instrumentation is simple and easy to operate. The time required for one determination is 15-20 minutes compared to 2.5 - 3 hours for existing method.

PUBLICATIONS:

Sekerka, I. and J.F. Lechner. 1992. Determination of Acid Volatile Sulfide in Fresh Water Sediments. Submitted for publication, proceedings of 4th Conference of Flow-Injection Analysis, Phoenix, Arizona.

STUDY NO.: **84014**

STUDY TITLE: **Broad Spectrum Analysis**

STUDY LEADER AND TEAM: **B.F. Scott, R. Sampson (NLET) and J.G. Zakrevski (WQB/WNR, Regina)**

INTRODUCTION: This study was initiated to optimize the information available from a sample after it has been analyzed using one or more detectors. In organic analysis, only target compounds are considered representing a fraction of the information available from an environmental sample. Using all the results available in the chromatogram will provide managers with a more comprehensive understanding of long term or upstream/downstream trends.

RESULTS: The two types of detectors selected for this study were the electron capture detector, controlled by an HP1000 computer with Real-Time-Executive software, and the atomic emission detector (AED) controlled by a Pascal Workstation. Previously, both report file types were reformatted, transferred electronically to a DOS environment, then placed in commercially available DOS based word processor and a DOS based spread sheet. With the latter, the results could be statistically evaluated or subjected to other chemometric techniques. During this reporting period, the objective was to overlay chromatograms of the same sample from the two instruments using a PC with a DOS environment. The chromatograms can now be overlaid, normalized and a hard copy produced. This is a major achievement.

To utilize the AED as a routine analytical tool, more investigations had to be conducted to augment work already completed. Since the response for each element is somewhat dependent on its environment, the ratio of one element to another in a series of similar compounds was determined. The calculated S/C and P/C ratios for a series of pesticides indicated that the response is variable. Therefore, extracts of natural water and sediment samples were chromatographed to ascertain the responses from the S, C, P, and N channels at the ppb level. The individual chromatograms for the elements S and C were at least as sensitive and as well resolved as those provided by other detectors.

PUBLICATIONS:

Scott, B.F., Y.K. Chau, and A. Rais-Firouz. 1991. Determination of Butyltin Species by GC/Atomic Emission Spectroscopy. App. Organomet. Chem. 5: 151-157.

STUDY NO.: **84016**

STUDY TITLE: **Operation of the Clean and Hazardous Chemicals Laboratory (CHCL) and Separation Procedures and Determination of Pollutants**

STUDY LEADER AND TEAM: **B.K. Afghan and R.J. Wilkinson**

INTRODUCTION: The purpose of this study is as follows: i) To provide specialized services to scientists conducting research and operational programs at CCIW and within DOE. The Laboratory (CHCL) is a unique facilities which is used to carry out analytical research at ultratrace levels, to serve as a containment facility for storing and preparing analytical standards of highly toxic and hazardous materials and to support DOE's initiative related to the pulp and paper industry. ii) To conduct research on separation methods for the quantitative and qualitative analysis of semi-polar and polar chemicals in the aquatic environment. The potential of LC-MS and the development of appropriate interfaces will be the focus for the next 2-3 years. This will enable scientists to study polar toxic chemicals in the environment and conduct ecotoxicological studies of polar toxins and study their mechanism of toxicity.

RESULTS: The following services were provided:

- Analytical standards of PCDDs and PCDFs were provided to the NLET, NWRI and DFO scientists at CCIW.
- Continued support was provided for QA/QC chlorinated dioxin/furan studies of RAB's Quality Assurance Project.
- Expertise and facilities were provided to Ms. J. Parrot of GLLFAS.
- Custom support was provided to Dr. R.L. Thomas of University of Windsor, Dr. Onuska of RAB and A. Mudroch of LRB.

Considerable work was also undertaken to evaluate the performance of the LC-MS system - TS 250/Tribrid in the GC-MS, GC-MS-MS and LC-MS modes. The instrument became operative and met the performance criteria at the end of February 1992. The system is currently being optimized with respect to the proper functioning of various interfaces and the suitability of solvent systems that are used in adsorption, normal phase and reverse phase chromatographic separations.

STUDY NO.: **84017**

STUDY TITLE: **Screening Techniques for Toxic Substances**

STUDY LEADER AND TEAM: **J. Sherry**

INTRODUCTION: Conventional methods for the analysis of trace organic contaminants in environmental samples tend to be time consuming and expensive. Screening techniques would greatly reduce analytical costs, by identifying contaminant free samples and eliminating the need for their subsequent quantitative analysis. Immunoassay (IA) screening techniques for trace organic contaminants are linked to the Green Plan and will support water quality monitoring programs in several regions.

RESULTS:

Triazine IAs: The optimization and validation of an enzyme-immunoassay (EIA) for atrazine was completed. The tube based EIA had detection limits of 62 pg/mL and 180 pg/mL of atrazine in lake and river water respectively. The assay's ability to quantify atrazine in water samples from many parts of Canada was compared with a GC-NPD reference method (R=0.919). A 71 % reduction in analytical load was achieved at a threshold concentration of 1 ng/mL.

Dioxin RIA: The radioimmunoassay (RIA) ability to detect 2,3,7,8-TCDD in crude animal and human plasma was evaluated and the assay was interfaced with an extraction and clean-up method. The assay's ability to detect 2,3,7,8-TCDD in serum extracts was assessed. The RIA could detect 10 pg of 2,3,7,8-TCDD in 100 μL of serum.

A broad range of co-planar and non co-planar PCBs (aroclors) did not cross react strongly in the RIA, although 2,3,7,8-chloroxanthene was highly reactive.

A trace analyte version of the monoclonal antibodies (MAB) based assay was developed, characterized, and optimized. Previous versions of the RIA for polychlorinated dibenzo-p-dioxins (PCDDs) used polyclonal antibodies. Among the advantages offered by MABs are stable specificity and affinity, unlimited supply, and generally steep dose response curves. The RIA used [^{3}H]-2,3,7,8-TCDD as a radio-ligand. Compared to its polyclonal equivalent, the MAB assay's curve was shifted to the left and had a lower ^{50}I value. The assay's estimated detection limit was 10 pg of 2,3,7,8-TCDD.

PUBLICATIONS:

Sherry, J.P. 1991. Radioimmunoassay for the Detection of Polychlorinated Dibenzo-p-Dioxins: [^{3}H]-2,3,7,8-TCDD Based Assay Version. NWRI Contribution No. 91-128.

Sherry, J.P. 1992. Environmental Chemistry: The Immunoassay Option. NWRI Contribution No. 92-03.

Sherry, J.P., J. Carron, D. Leger, J. Kohli, and R.J. Wilkinson. 1992. An MSD-based Method for the Detection of Chlorinated Dibenzo-p-Dioxins and Chlorinated Dibenzofurans in Fish. NWRI Contribution No. 92-12.

Sherry, J.P. and A. Borgmann. 1992. Enzyme-Immunoassay Techniques for the Detection of Atrazine in Water Samples: 1. ImmunoSystem's Tube Based Assay. NWRI Contribution No. 92-13.

Sherry, J.P. and A. Borgmann. 1992. Tube Based Enzyme-Immunoassay for Triazine: Method Description. NWRI Contribution No. 92-14.

PRESENTATIONS:

Sherry, J.P., L. Stanker, B. Watkins, M. Vanderlaan, and P. Albro. "Monoclonal antibody based radioimmunoassay for the detection of polychlorinated dibenzo-p-dioxins". Presented at the Dioxin '91 Conference, Raleigh/Durham, North Carolina, September 23-27, 1991.

TECHNOLOGY TRANSFER:

Transferred a previously developed dioxin clean-up method to NOVA labs in Montreal. The immunoassays for dioxins and triazines are available for transfer to receptive clients.

STUDY NO.: **84018**

TITLE OF STUDY: **Development and Application of Methods for Organic Compounds**

STUDY LEADER & TEAM: **H.B. Lee, and T.E. Peart**

INTRODUCTION: Conventional extraction techniques for organics in sediments are tedious and produce large quantities of waste solvents which create a disposal problem. New techniques involving supercritical fluid extraction (SFE) with carbon dioxide are potentially more efficient and environmentally friendly. Development of analytical methods for priority pollutants (CEPA, GLWQA) and pulp mill contaminants (Green Plan, CEPA) using SFE is therefore required for NWRI and NLET programs.

RESULTS: In our continuing research for analytical methods for organic contaminants, we have developed a method for the determination of resin and fatty acids in sediments at pulp mill locations using a supercritical carbon dioxide extraction technique. The extraction was not only faster than the conventional Soxhlet procedure, it also produced better recovery for some unstable acids and was nearly solvent-free. Another SFE method for the determination of pentachlorophenol and related chlorophenols in soils from a wood preservation site was also developed. This method involved a one-step, in situ extraction/acetylation approach for a further reduction in sample preparation time. Extraction of priority pollutants such as chlorobenzenes, PCBs, and PAHs from sediments using supercritical carbon dioxide has also been investigated. The results indicated that SFE was the method of choice for the extraction of most organics from sediments.

PUBLICATIONS:

Lee, H.B. and T.E. Peart. 1991. Supercritical Carbon Dioxide Extraction of Resin and Fatty Acids from Sediments at Pulp Mill Sites. NWRI Contribution No. 91-123. J.Chromatogr. 594: 309-315 (1992).

Lee, H.B., T.E. Peart, and R.L. Hong-You. 1992. In Situ Extraction and Derivatization of Pentachlorophenol and Related Compounds from Soils Using a Supercritical Fluid Extraction System. NWRI Contribution No. 92-01. Accepted for publication, J. Chromatography.

Lee, H.B., T.E. Peart, and R.L. Hong-You. 1992. A New and Improved Method for the Determination of Chlorobenzenes and Hexachloro-1,3-butadiene in Sediments Using Supercritical Carbon Dioxide Extraction. NWRI Contribution No. 92-08.

Niimi, A.J. and H.B. Lee. 1992. Free and Conjugated Concentrations of Nine Resin Acids in Rainbow Trout (Oncorhynchus mykiss) Following Waterborne Exposure. In press, Environmental Toxicology and Chemistry.

STUDY NO.: **84019**

STUDY TITLE: **Spectrometric Techniques for Environmental Analysis**

STUDY LEADER AND TEAM: **V. Cheam, I. Sekerka, J.F. Lechner and R. Desrosiers (RSB)**

INTRODUCTION: The purpose of the study is to develop a laser-based ultrasensitive instrument and method to permit direct analysis of water samples containing very low levels of Pb such as the Great Lakes waters. Existing graphite furnace AAS or ICP methodologies require sample preconcentration by such procedure as solvent extraction/ backextraction or evaporation. These steps are not only time consuming and labour intensive but are also prone to contamination and tend to give biased high results. For accurate determination of ultratrace amounts of metals, there is an obvious need to develop a very sensitive technique and an effective method to alleviate these problems. This need is in direct accord with the ESED mandate, to constantly improve analytical capability.

RESULTS: An ultrasensitive Laser-Excited Atomic Fluorescence Spectrometer (LEAFS) has been successfully constructed. A Copper Vapour Laser-pumped Dye Laser along with many other high-tech instruments form part of this LEAFS. It is the first one in Canada to be successfully applied to the analysis of environmental samples.

A novel, simple and practical method for tuning dye lasers has been successfully developed and used routinely. The method uses two common laboratory items, a pierced mirror and an electrodeless discharge lamp. In contrast to the conventional procedure using flame, there are no nebulizer-burner, hood, gas tanks, nor burner control unit involved. Thus our tuning system is also cost-effective and discharges no metal atoms into the environment.

An analytical method using LEAFS has been developed for the **direct** analysis of Great Lakes water samples for lead. A detection limit of 0.4 ppt (10 fg absolute) was derived. The generation of data is simple and straightforward compared to conventional methods, which need preconcentration steps before analysis can be made. The LEAFS method avoids biased high results, which the conventional methods tend to produce. To our knowledge, this is the first time that the direct analyses of such samples have ever been successfully performed.

PUBLICATIONS:

Cheam, V. 1991. Isocratic Anion Chromatography Method and Comparison of Methods for the Determination of Organic and Inorganic Acids in Precipitation Samples. NWRI Contribution No. 91-129.

Cheam, V., R. Desrosiers, J. Lechner, and I. Sekerka. 1991. A Novel, Simple Method for Tuning Dye Lasers. NWRI Contribution No. 91-125. Accepted for publication in Microchemical Journal.

Cheam, V. 1991. Isocratic Anion Chromatographic Method and Comparison of Methods for the Determination of Organic and Inorganic Acids in Precipitation Samples. NWRI Contribution No. 91-129. Accepted for publication, The Analyst.

Cheam, V., J. Lechner, I. Sekerka, R. Desrosiers, J. Nriagu, and G. Lawson. 1992. Development of a Laser-Excited Atomic Fluorescence Spectrometer and a Method for Direct Analysis of Pb in Great Lakes Waters. NWRI Contribution No. 92-05.

PRESENTATIONS:

Cheam, V., I. Sekerka, J. Lechner and R. Desrosiers. "A Novel Procedure for Tuning Dye Lasers Used in Laser-Excited Atomic Fluorescence Spectrometry (LEAFS)". Presented at the 37th Canadian Spectroscopy Conference, Ottawa, Ontario, August 12-14, 1991.

TECHNOLOGY TRANSFER:

Provided Pb reference data generated by LEAFS method to Dr. J. Nriagu (LRB) for 30 water samples from Lakes Ontario, Erie and Superior, as well as for many extraction solutions he used to test extraction efficiency of various preconcentration procedures.

Provided Pb reference data generated by LEAFS method to H. Wong for his many reference waters for ultratrace levels.

Identified and quantitated a contamination problem for NLET.

QUALITY ASSURANCE

STUDY NO.: **84021**

STUDY TITLE: **Organic Quality Assurance**

STUDY LEADER AND TEAM: **Y.D. Stokker and A.S. Y. Chau**

INTRODUCTION: The Organic QA study designs, conducts, and provides interpretation of interlaboratory studies in support of the Canadian Association of Pesticide Control Officials (CAPCO), the National QA Program, the Federal/Provincial Agreements, and the National Dioxin QA Program. In addition, research is conducted on the preparation and development of reference materials in the form of analytical standard solutions, sample extracts, and natural substrates.

RESULTS: Three organic interlaboratory studies were conducted this year. In the 1991 CAPCO QC Study, the majority of the 29 participating laboratories provided accurate results and good comparability for the nine acid herbicides in sediment extracts and standard solutions. The second study, Federal/Provincial Interlaboratory QA Study No.4, was conducted on the analysis of eighteen PAHs in ampules. Only one of the 14 participants had any significant analytical problems. The third study, National Dioxin Interlaboratory QC Study No.4, involved thirteen laboratories analyzing four freeze-dried, naturally-contaminated reference sediments for 2,3,7,8-TCDD, 2,3,7,8-TCDF, and the tetra- to octachlorinated dioxin and furan homologue totals. Most of the data showed considerable improvement from previous dioxin QA studies. Several participants, however, continued to produce biased data, particularly for the analysis of some of the furans.

Funded by the Pesticide Multi-Year Operational Plan program, a reference sediment extract of Lakes Erie and St. Clair sediment was fortified with 9 acid herbicides (AHs). 'Standard' solutions were also prepared to compliment the concentration levels in this sediment extract. Homogeneity of these ampules was confirmed and the stability of the AHs was verified over a six-month period.

The sediment Reference Materials (RMs) and Certified Reference Materials (CRMs) were again analyzed this year to verify the stability of the PAHs, PCBs, and chlorobenzenes therein. No signs of any losses of these contaminants were detected. Cost-recovery sales of the sediment RMs and CRMs for the past fiscal year totalled about $6K.

PUBLICATIONS:

Stokker, Y.D., E.A. Kokotich and A.S.Y. Chau. 1991. National Dioxin Interlaboratory Study No.1 on the Analysis of Dioxins and Furans in Sediment. NWRI Contribution No. 91-113.

Stokker, Y.D. and E.A. Kokotich. 1991. National Dioxin Interlaboratory Study No.2 on the Analysis of Dioxins and Furans in Sediment. NWRI Contribution No. 91-119.

PRESENTATIONS:

Stokker, Y.D. "Quality Assurance and Certified Reference Materials". Presented at the 23rd Eastern Canada Pesticide Workshop, Moncton, New Brunswick, May 28-30, 1991.

TECHNOLOGY TRANSFER:

QA/QC advice was provided to the following: (i) CAEAL on the design of the first organic study in the CAEAL certification program; (ii) WQB/OR on the preservation of neutral and acid herbicides in natural waters; (iii) Indian and Northern Affairs Canada, Litigation Support Directorate on laboratory performance; and (iv) NLET on concentration techniques for chlorobenzene analysis.

STUDY NO.: **84022**

STUDY TITLE: **Federal/Provincial Quality Assurance Program**

STUDY LEADER AND TEAM: **H.A. Alkema, K.I. Aspila and Y.D. Stokker**

INTRODUCTION: This study, since the early 1980's, has supported the Federal-Provincial Quality Assurance Program by assessing the quality of data created by federal and provincial laboratories in Canada. Intercomparison studies are provided bimonthly to over 30 different laboratories for analysis of over 40 different constituents in paired water samples. These constituents include major ions, nutrients, physical parameters and trace metals. Results are evaluated by flagging results that deviate significantly from target values. The relative performance of the thirty different laboratories is compared in a tabulation of the frequency of flagged data. There are several laboratories that consistently provide a very high frequency of flagged data.

RESULTS: In the past year, 6 regular interlaboratory studies were designed with typical regional waters from Ontario and the Prairie Provinces. These studies were sent to the 30 participants who promptly returned analysis results. After evaluation of deviant and outlying results, an evaluation and a final report were promptly sent to each laboratory so that remedial action could be taken to correct problems or systematic errors.

The analytical results for all studies are maintained on a data base management system maintained by the NWRI computer Group on their mainframe Cyber computer. During the past year, this system has been modified and upgraded to the ORACLE data base. This system will now be used to perform all evaluations, to keep track records on the performance of each laboratory, and to process and create laboratory specific appraisals.

Because this ongoing program began as a small internal Environment Canada analysis check, and because this type of study design cannot meet current systematic and diagnostic needs, a proposal has been submitted to improve the study design. When implemented, the new intercomparison studies will lead to a more effective interpretation of data and more specific information to allow each laboratory to improve their laboratory performance.

STUDY NO.: **84023**

STUDY TITLE: **LRTAP Interlaboratory Quality Assurance Studies**

STUDY LEADER AND TEAM: **K.I. Aspila, and N. Arafat**

INTRODUCTION: This project provides a laboratory audit function that helps to define the credibility of those laboratories that create data for acid rain programs in Canada and the United States. These interlaboratory studies address the quality of data for major ions, nutrients and physical parameters in soft surface waters and rain water. The popularity of this program has increased the number of laboratories from 32 in 1982 to over 131 in 1992.

RESULTS: During this fiscal year, three intercomparison studies, L27, L28 and L29 were designed, developed, delivered and evaluated. These studies included ten test samples that were provided to an average of 65 different laboratories in Canada and the United States. Results were evaluated for laboratory bias by the nonparametric technique of Youden. Individual laboratory results that deviated from interlaboratory median values were flagged as high or low.

Results of all studies are maintained on a data base management system. This allows for an analysis of data over time to produce a definition of performance referred to as the track record of each laboratory. This assessment of performance is based on the frequency of bias and of flagged data. The data base continues to illustrate how laboratories can improve when monitored by an effective ongoing interlaboratory study program.

STUDY NO.: **84024**

STUDY TITLE: **Quality Assurance For Atmospheric Toxic Organics**

STUDY LEADER AND TEAM: **A.S.Y. Chau, K.I. Aspila and D.H.J. Anthony**

INTRODUCTION: This project in FY 91/92 focused on the accumulation of rainwater in order to acquire a large sample sufficient to create an extract suitable for use in monitoring the performance of those laboratories analyzing toxic organics in precipitation within the Great Lakes Basin.

RESULTS: A greenhouse in Grimsby Ontario was modified to allow rainfall to be captured off a 900 square foot glass surface into five 200 litre stainless steel barrels. During the course of the summer three rainfall events were captured and shortly after each event the 1000 litre units of rainwater were extracted into dichloromethane. By late summer, preliminary analysis indicated that the samples collected contained traces of toxic organics. The extracts, maintained in cold storage at CCIW are now available for use in an intercomparison study.

During the course of the fiscal year, ampuled standards for 16 different polyaromatic hydrocarbons, several pesticides, a variety of chlorobenzenes and PCB's were prepared as analytical reference standards. Some of these standards were provided to an atmospheric research scientist for a small intercomparison study. An inventory system was developed to control this stockpile of several hundreds of ampuled standards. The design values and the stability under current storage conditions are being confirmed. These ampuls will be used in forthcoming intercomparison studies.

In the winter of 1991/92, the project staff proposed a comprehensive QA study to the Bilateral Atmospheric Work Group. It was agreed, under the circumstances that developed over the previous years, that the more comprehensive study would occur in FY 92/93, after a review of the small study set up earlier by the Bilateral Work Group.

This next phase in this study will proceed when the coordination aspects from the atmospheric QA committee are finalized.

STUDY NO.: **84025**

STUDY TITLE: **External Quality Assurance Studies**

STUDY LEADER AND TEAM: **K.I. Aspila, H.A. Alkema, K. Ranstoller and C. Vogel**

INTRODUCTION: This project provides a Quality Assurance support service, through contractual arrangements with the Province of British Columbia (BC), the Atmospheric Environment Service (DOE Downsview) and the Canadian Association of Environmental Analytical Laboratories (CAEAL). The support includes interlaboratory studies and the provision of audit samples for laboratory performance evaluations.

RESULTS: For the Atmospheric Environment Service (AES) over 1000 pH audit control samples (pH = 4.235) were provided to monitor the six laboratories that create data for the AES Rain Project. In addition a pH kit (consisting of 5 pH standards) was developed and supplied to AES for intercalibrating the six rain laboratories.

For the CAEAL Accreditation Program, QA studies were provided in September 1991 and March 1992. The studies involved 60 laboratories, and included total phosphorus, TKN, major ions, nutrients, physical parameters and trace metals in water.

For the BC Ministry of the Environment accreditation studies, QA studies were distributed in September 1991 and in March 1992. The studies involved about 60 laboratories which were provided test samples for total phosphorous in sewage plant effluents and major ions, TKN, nutrients, physical parameters and trace metals in water.

PRESENTATIONS:

Aspila, K.I. "On the Impact of an Effective External Quality Assurance Program". Presented at the following:

(i) Chemical Institute of Canada, CAEAL Symposium, Hamilton, Ontario, June, 1991;
(ii) National Conference of Standards Laboratories, Canada Centre for Inland Waters, Burlington, Ontario, November, 1991;
(iii) Department of Energy Mines and Resources, Geological Surveys of Canada, Ottawa, Ontario, July, 1991;
(iv) Chalk River Nuclear Laboratories, Chalk River, Ontario, July, 1991;
(v) Laboratory Services Branch, Environment Ontario, "Quality Assurance Day Meetings", Rexdale, Ontario, August, 1991; and
(vi) Quality Assurance Work Group Meeting, (Canada - BC), Victoria, B.C., November, 1991.

STUDY NO.: **84027**

TITLE OF STUDY: **CEPA Quality Assurance**

STUDY LEADER & TEAM: **W.C. Li, A.S.Y. Chau and C. Chiu (RRETC, Ottawa)**

INTRODUCTION: In support of the Canadian Environmental Act (CEPA), a CEPA QA program has been established for regional and national monitoring and assessment of toxic contaminants. The major objectives of this study were to implement interlaboratory studies and to develop reference materials for toxic organics.

RESULTS: An interlaboratory study (CP-3) on the determination of dioxins and furans in sediment extracts was designed and completed in support of the CEPA program. The data evaluation is now in progress. In response to EP-Ontario Region, a QA/QC program for sediments was initiated in September, 1990. In FY 91/92, two interlaboratory studies (Studies No. G-2 and G-3) for the determinations of octachlorostyrene (OCS), and chlorobenzenes (CBs) in sediments were designed and completed. Preliminary data summaries have been prepared and distributed to participating laboratories. The summaries provided information on the comparability of a laboratory with its peers and on the comparability of submitted resulted with the design values.

To support the various interlaboratory studies of the CEPA QA program, several reference samples of different characteristics were required. Two sediment reference materials, namely EC-2 and EC-3 were developed for dioxins and furans. While another two sediment reference materials, EC-6 and EC-7, were developed for OCS and CBs. In addition, two sediment extract reference samples were also prepared from the bulk sediment reference materials of EC-7 and EC-8 for OCS and CBs, and for dioxins and furans, respectively. Some preliminary results for the above-mentioned sediment reference samples have been obtained from in-house analysis and various interlaboratory studies.

PUBLICATIONS:

Li, W.C., A.S.Y. Chau and I. Orchard. 1991. Interlaboratory Study No. G-1: Analysis of Selected Chlorinated Hydrocarbons in Sediments. NWRI Contribution No. 91-127.

Zhang,S., Y.K. Chau, W.C. Li and A.S.Y. Chau. 1991. Evaluation of Extraction Techniques for Butyltin Compounds in Sediment. NWRI Contribution No. 91-54. Appl. Organomet. Chem. 5: 431-434.

HYDRAULICS

STUDY NO.: **84030**

TITLE OF STUDY: **Impact of Tire Leachate on the Aquatic Environment**

STUDY LEADER & TEAM: **C.T. Bishop, B.K. Afghan, F. Yang (Carleton Univ. Ottawa), K. Day (RRB) and J. Smith (RRB)**

INTRODUCTION: This study aims to assess the toxicity of leachate from several types of car tires, and to identify toxic chemicals (if any) in the leachate. This relates to Green Plan initiatives on toxics and on managing waste.

RESULTS: A multidisciplinary study initiation meeting was held in September 1991. A contract study (partially funded by Fisheries and Habitat Management, DFO) was awarded to BAR Environmental Ltd. to conduct toxicity tests of leachate from three types of car tires in freshwater: brand new tires (never on the road), tires used on an average passenger car for 4 years, and scrap tires that had been part of a floating tire breakwater for over 10 years. It was found that leachate from the new and used tires, but not from the scrap tires, is toxic to rainbow trout but not to fathead minnows or Daphnia magna. The toxicity is persistent and nonvolatile. Samples of the tire leachate were brought to NWRI where they have been extracted and stored in a cold room.

Another contract was awarded to Carleton University to allow a graduate chemistry student, Fan Yang, to conduct a literature search on the chemistry and toxicity of tires in water. He will also work at NWRI from May to August 92 to conduct chemical identification tests on tire leachate.

PUBLICATIONS:

BAR Environmental Ltd. Guelph, Ontario. 1992. Evaluation of the Potential Toxicity of Automobile Tires in the Aquatic Environment.

TECHNOLOGY TRANSFER:

Several other agencies showed strong interest in the progress of these tests. They include F&HM (DFO), the Waste Management Branch of the Ontario Ministry of the Environment, the Marine Forests Society (a non-profit corporation in California proposing the use of scrap tires for mariculture habitat) and Saskatchewan Parks and Renewable Resources (who experienced a recent controversy over the alleged toxicity of an artificial tire reef). Communication with these agencies, as well as with rubber associations, is ongoing.

STUDY NO.: **84031**

TITLE OF STUDY: **The Surface Wave Dynamics Experiment (SWADE)**

STUDY LEADER & TEAM: **M.A. Donelan, W. Drennan and D. Beesley**

INTRODUCTION: The effect of waves on the atmosphere-ocean/lake couplings for transfer of mass, momentum and energy and the resultant importance of these processes to weather prediction and climate change are now generally recognized. The Surface Wave Dynamics Experiment (SWADE) was conceived with the primary goals of understanding the dynamics of the evolution of the wave field in the open ocean/lake, and determining the effect of waves on the air-sea transfer of momentum, heat and mass.

RESULTS: This year was spent on intensive analysis of SWADE data and coordination of the many research teams within SWADE. The analysis of the directional wave spectra from the SWATH ship and of the high resolution Maximum Likelihood Method for the NDBC buoys is complete. Several papers have been written already using the SWADE data base. The guide to the extensive SWADE data base is currently being prepared. This will permit all SWADE investigators to make maximum use of all data systems.

PUBLICATIONS:

Huang, N.E., S.R. Long, Chi-Chao Tung, M.A. Donelan, Y. Yuan and R.J. Lai. 1992. The Local Properties of Ocean Surface Waves by the Phase-Time Method. NWRI Contribution No. 92- . Submitted to Geophysical Research Letters.

O.M. Phillips, Daifang Gu and M.A. Donelan. 1991. On the Expected Structure of Extreme Waves in a Gaussian Sea, 1. Theory and SWADE Buoy Measurements. NWRI Contribution No. 91-131. In press, J. Physical Oceanography.

Anctil, F., M.A. Donelan, G.Z. Forristall, K.E. Steele and Y. Ouellet. 1991. Deep Water Field Evaluation of NDBC/SWADE 3-Meter Discus Directional Buoy. NWRI Contribution No. 91-122. In press, J. Atmospheric & Oceanic Technology.

Donelan, M.A., W.M. Drennan, K.B. Katsaros, E.A. Terray and C.N. Flagg. 1992. Directional Spectra from the SWATH ship in SWADE. NWRI Contribution No. 92-11.

Anctil, F. and M.A. Donelan. 1991. Eddy Correlation Measurements of Air-Sea Fluxes. Submitted for publication, J. Atmospheric & Oceanic Technology.

STUDY NO.: **84032**

TITLE OF STUDY: **Fluvial Engineering**

STUDY LEADER & TEAM: **P. Engel, Y.L. Lau (RRB), B.G. Krishnappan (RRB), I.G. Droppo (RRB), J. Fulford (USGS, Stennis Space Centre, Miss.), W. Kaehrle (USGS, Stennis Space Centre, Miss.)**

CLIENTS: **K. Wiebe (WRB, Ottawa), P. Zrymiak (WRB, Ottawa), B. Tassone (WRB, Vancouver), M.O. Spitzer (WRB, Calgary)**

INTRODUCTION: Work is directed at research and applications of fluid mechanics, sediment transport in rivers, development of techniques for monitoring river process and flow-structure interaction. Emphasis is placed on providing information for operational branches in Environment Canada, especially the Surveys and Information Systems Branch (SISB). Results are applicable to issues in other departments and available to other water resources managers.

RESULTS: The development of quality control criteria for discharge measurements in rivers for SISB continued and focussed on the calibration of current meters. It was found that the uncertainty of the calibrations is a function of the calibration process itself. Work on the application to flow measurements in rivers with solid ice cover of a three-dimensional numerical model was conducted jointly by RAB, RRB and SISB. Preliminary results indicate that a combination of numerical models and measurements can be an efficient combination for determining discharge in rivers with ice cover. The development of a comprehensive strategy for the calibration of suspended sediment samples, used nationally by SISB, proceeded as planned. Tests on the uncertainty in the performance of all types of suspended sediment samplers used by SISB continued. An efficient and economical stilling basin to prevent scour downstream of the Milk River weir was developed with the aid of hydraulic model tests. The study showed that a simple rip-rap apron, using locally available rocks, is a satisfactory means of protecting the weir from excessive scour.

Work on analyzing the extensive data from sediment transport tests conducted in the two metre flume in the Hydraulics Laboratory continued. Careful review of the literature revealed anomalies in present methods used to analyze sand grain roughness and form roughness of sand waves. Work is underway to develop more reliable procedures to determine these two components of the friction factor for such applications as numerical modelling of the Fraser River. Theoretical analysis of the performance characteristics of large volume suspended sediment samplers shows that the sample catch is strongly dependent on the ratio of air vent diameter to nozzle diameter. Data from extensive tests confirm this.

A model study to assist Gore and Storrie, Consulting Engineers, in the design of a free surface surge tank and de-foaming chamber was completed. A report was presented to the client.

PUBLICATIONS:

Engel, P. 1991. Preliminary Examination of the Uncertainty in the Repeatability of the Price Meter Calibrations. NWRI Contribution No. 91-116.

Engel, P. 1991. Basic Requirements for Iso-Kinetic Operation of Large Volume Point Integrating Sediment Samples. NWRI Contribution No. 91-120.

Engel, P. and J. Marsalek. 1991. Hydraulic Model Study of Flow Conditioning Alternatives for a Free Surface Head Tank. RAB Contract Report No. 91-19.

Engel, P. and I. Droppo. 1992. Effects of Nozzle and Air Vent Size on Sediment Sampler Performance. NWRI Contribution No. 92-06.

TECHNOLOGY TRANSFER:

P. Engel has been appointed as a member to the Standard Council of Canada's Canadian Advisory Committee for the International Organization for Standardization's Technical Committee 113 - Measurement of Liquids in Open Channels. The scope of this committee is the standardization of rules and methods relating to measurement of liquid flows with particular reference to sediment transport in open channels. This appointment provides an important link to strengthen the support provided to SISB by the Hydraulics Laboratory.

STUDY NO.: **84033**

STUDY TITLE: **Coastal Engineering**

STUDY LEADER AND TEAM: **M.G. Skafel, C.T. Bishop, M.A. Donelan, J. Doering, R. Nairn**

INTRODUCTION: Physical processes in the coastal zone, which are in the realm of coastal engineering, have a direct bearing on many ecosystem issues. Shoreline evolution is of direct relevance to the programmes of the Water Planning and Management Branch (WPMB). We are currently examining the erosion of till (clay) shores, which are of particular interest to the WPMB Ontario Region's concerns in the Great Lakes. Suitable design criteria for coastal structures is vital to minimize environmental risks. Recent activities have dealt with improved wave descriptions for structural loading, in support of the Interdepartmental Panel on Energy Research and Development (PERD).

Cohesive Shoreline Modelling

Introduction: Much of the lower Great Lakes shoreline is composed of glacial till, so that an understanding of the erosion by waves and the associated effects of varying lake levels on cohesive shorelines is important to Great Lakes shoreline management. Large scale wave flume facilities in the Hydraulics Laboratory make possible the physical hydraulic modelling of this process which, until now, has not been done.

Results: Laboratory testing continued throughout the year. Preliminary tests were completed with two water depths, with and without sand , and with the addition of a revetment. A substantial scour hole developed near the mean water level, which coincided with a region of plunging wave breaking. Elsewhere on the profile, very little erosion was evident in the absence of added sand. When a thin veneer of sand was present on the till, erosion was accentuated. More sand, enough to form a bar, resulted in a protected zone under the bar. When the revetment was placed on the profile, a scour hole developed at the toe of the bar. The profile was rebuilt and at year-end tests are continuing to validate the results from the first series.

Technology Transfer: The preliminary results have been used by a consultant as resource material and to provide partial calibration of a numerical model in a project to estimate effects of water level regulation for the International Joint Commission.

Shoaling Waves

Introduction: In applying the concept of sustainable development to coastal and offshore structures it is apparent that the chance of damage to the environment must be minimized. Waves cause the main loads to structures and are inherently random in nature. A succinct description of the joint distribution of wave heights and periods in shoaling water is vital to designs, and is the goal of this work. It is supported by PERD.

Results: Data from field and laboratory experiments in shoaling water have been compared to a deep water model of Longuet-Higgins; significant differences emerge in quite shallow water which will have an influence on the design of structures.

PUBLICATIONS:

Doering, J. C. and M.A. Donelan. 1991. The Evolution of the Joint Probability Density Function of Wave Height and Period During Shoaling. NWRI Contribution No. 91-126.

Bishop, C.T., M.A. Donelan, and K.K. Kahma. 1992. Shore Protection Manual's Wave Prediction Reviewed. Coastal Engineering 17: 25-48.

Skafel, M.G., C.T. Bishop, and R.B. Nairn. 1992. Erosion of Till Shores by Waves. Abstract accepted, IAGLR Conference, Waterloo.

Bishop, C.T., M.G. Skafel, and R.B. Nairn. 1992. Cohesive Profile Erosion by Waves. Abstract accepted, 23rd International Conference on Coastal Engineering, Venice.

STUDY NO.: **84034**

TITLE OF STUDY: **Physics of the Air-Water Interface**

STUDY LEADER & TEAM: **M.A. Donelan, W. Drennan and D. Beesley**

INTRODUCTION: This study is focussed on fundamental processes related to the air-water interface, particularly topics such as surface waves, interfacial transport of mass, momentum and energy, wave related forces, and effect of breaking waves on surface mixing.

RESULTS: This year the research into the "Physics of the Air-Water Interface" has focussed on several key areas:

(1) Wave breaking and the consequent distribution of a turbulent kinetic energy dissipation in the near surface waters.
(2) The structure of wave induced velocities in a wind-sea and agreement with linear theory.
(3) Wave growth at limited fetch and approaches to full development.
(4) The wind stress on water bodies.
(5) The effect of shoaling of random waves on their joint probability density of heights and periods.
(6) The propagation of water-wave groups.

The work in these areas has been in collaboration with other RAB staff and scientists from 11 different institutions in Canada, U.S., Europe and Australia. A brief synopsis of the work follows:

(i) *Wave breaking:* The data from the WAVES experiment on NWRI's Lake Ontario tower led to new insight into the enhancement of turbulent kinetic energy dissipation in the surface waters beneath breaking waves. This work has important repercussions for upper layer mixing, diffusion of surface waters and gas transfer.

(ii) *Wave induced velocities:* Again the WAVES experiment provided the data to assess linear theory estimates of the velocity structure beneath wind-waves. The results are encouraging for the engineering use of linear theory if properly applied. Another aspect of this work led to the formulation of a new method for calculating the velocity field beneath wind-waves from surface to bottom. Previous methods relied on ad hoc adjustments to linear theory.

(iii) *Wave growth:* In one part of this work we corrected some serious errors in the methodology expressed by the best regarded engineering guide to coastal engineering. In another, we used our own data (obtained jointly with the U.S. Great Lakes Environmental Laboratory) from Lake St. Clair to devise a new fetch-limited growth "law" that is contingu[illegible]s to established ideas on full development.

(vi) *Wind s[illegible]ss:* In a review paper for a conference on "Strategies for Future Climatic Research" the history of parameterization of the drag of the wind on water bodies was summarized. In addition, the importance of short waves, in the dual task of

communicating the stress and in providing the necessary signal to satellite remote sensing devices for surface winds, was recognized.

(v) *Shoaling waves:* In this PERD supported study, the changes in the distribution of heights and periods as waves shoal was investigated in laboratory and field. This information is of great value to coastal engineers working with hindcasted storms in deep water.

(vi) *Wave group propagation:* The group structure of wind-waves has important dynamical consequences on the loading of offshore structures and the mooring of ships. It may also be a key element of the breaking process and in the mechanics of wave generation. For this laboratory study, various aspects of the linear and non-linear propagation of groups are investigated. The results verify some existing theories and bring out the shortcomings of others.

PUBLICATIONS:

Banner, M.L. and M.A. Donelan. 1991. The Physical Consequences of Wave Breaking in Deep Water. NWRI Contribution No. 91-132. Proceedings of IUTAM "Breaking Waves" Symposium, Sydney.

Drennan, W.M., K.K. Kahma, E.A. Terray, M.A. Donelan and S.A. Kitaigorodskii. 1991. Observations of the Enhancement of Kinetic Energy Dissipation Beneath Breaking Wind Waves. Proceedings of IUTAM "Breaking Waves" Symposium, Sydney.

Agrawal, Y., E.A. Terray, M.A. Donelan, P.A. Hwang, A.J. Williams III, W.M. Drennan, K.K. Kahma and S.A. Kitaigorodskii. 1992. Enhanced Dissipation of Kinetic Energy Beneath Surface Waves. NWRI Contribution No. 92-04. In press, Nature.

Drennan, W.M., K.K. Kahma and M.A. Donelan. 1991. The Velocity Field Beneath Wind-Waves. NWRI Contribution No. 91-118. In press, Coastal Engineering.

Donelan, M.A., F. Anctil and J.C. Doering. 1992. A Simple Method for Calculating the Velocity Field Beneath Irregular Waves. Coastal Engineering 16: 399-424.

Bishop, C.T., M.A. Donelan and K.K. Kahma. 1991. Shore Protection Manual's Wave Prediction Reviewed. Coastal Engineering 17: 25-48.

Donelan, M.A., M.G. Skafel, H. Graber, P. Liu, D. Schwab and S. Venkatesh. 1992. On the Growth Rate of Wind-Generated Waves. NWRI Contribution No. 91-117. In press, Atmos-Ocean.

Donelan, M.A. 1991. The Mechanical Coupling Between Air and Sea - An Evolution of Ideas and Observations. NWRI Contribution No. 91-124. Proceedings of a Symposium on Strategies for Future Climate Research, Hamburg, Germany.

Doering, J.C. and M.A. Donelan. 1991. The Evolution of the Joint Probability Density Function of Wave Height and Period During Shoaling. NWRI Contribution No. 91-126. Proceedings 2nd Caribbean Conference on Fluid Dynamics.

Pierson, W.J., M.A. Donelan and W.H. Hui. 1992. Linear and Nonlinear Propagation of Water Wave Groups. J. Geophys. Res. 97(4): 5607-5621.

TECHNOLOGY TRANSFER:

A computer program has been prepared to calculate the velocity field beneath random waves. The program has been offered for sale to the general public. Several requests have been received.

STUDY NO.: **84035**

TITLE OF STUDY: **Transfer of Toxic Gases**

STUDY LEADER & TEAM: **M.A. Donelan, F.J. Ocampo-Torres, M. Alaee, D. Beesley and W. Strachan**

INTRODUCTION: Understanding and estimating gas transfer at air-water interfaces are critical aspects considered in studies on the fate of anthropogenic pollutants in the environment. Very little useful analysis of the transfer of synthetic organic substances of moderate molecular weight has been reported in the literature. This is partly because relevant studies of this process require a combination of physical and chemical methods and measurements as well as access to laboratory facilities appropriately designed and equipped for this kind of research. NWRI has supported under this study the design and construction of a modern gas transfer wind-wave facility.

RESULTS: Detailed measurements of the mass transfer of water vapour and carbon dioxide have been made using a Non-Dispersive Infra-red Analyser. The results are of unprecedented quality (< 0.3% error) and reveal interesting changes in the physics of the gas transfer process as the wind speed is increased from 0 to 16 m/s in the gas transfer flume. Preparations are nearly complete to extend the methods used to a wider range of environmental pollutants using the Fourier Transform Infra-red Analyser.

PUBLICATIONS:

Ocampo-Torres, F.J. and M.A. Donelan. 1991. Drift Velocity Profiles as Inferred from Measurements of Surface Wave Celerity. NWRI Contribution No. 91-114. Submitted for publication, J. Physical Oceanography.

Ocampo-Torres, F.J., M.A. Donelan, N. Merzi and F. Jia. 1991. Laboratory Measurements of Mass Transfer of Carbon Dioxide and Water Vapour for Smooth and Rough Flow Conditions. NWRI Contribution No. 91-130. Submitted for publication, Tellus.

Ocampo-Torres, F.J. and M.A. Donelan. 1991. Exploring the Upper Decimeter of a Wind Driven Water Body. NWRI Contribution No. 91-115.

STUDY NO.: **84036**

TITLE OF STUDY: **National Calibration Study**

STUDY LEADER & TEAM: **W.B. Taylor, D. Fekyt, C. Bil, B. Near and G. Voros**

INTRODUCTION: This study encompasses NWRI's continuing commitment to calibrate and maintain all flow meters owned and used by the Monitoring and Survey Division (Survey and Information Systems Branch, Environment Canada). This work is organized and conducted through the National Calibration Service.

In addition to the services provided to the Monitoring and Survey Division, the National Calibration Service provides calibration and instrument repair services to outside clients on a cost recovery basis. Revenue generated assists in funding maintenance costs of the facility.

RESULTS: For 1991-92, 185 requests for services were actioned. A total of 807 calibrations and 440 current meter repairs were completed for the Monitoring and Survey Division offices throughout the country, as well as for universities, provincial departments, other federal departments, hydro utilities and private companies. These requests have resulted in revenues of $35.5K for this fiscal year.

STUDY NO.: **84037**

TITLE OF STUDY: **Hydraulics and Sedimentology Laboratory Operations**

STUDY LEADER & TEAM: **W.B. Taylor, Technical Services Staff, M.G. Skafel, J.P. Coakley (LRB) and D. Delorme (LRB)**

INTRODUCTION: This study provides for specialized technical support staff and fully operational laboratories and equipment for hydraulics, rivers, and geotechnical research and related field activities. Within this study, requests for technical services are coordinated and laboratory facilities and equipment are maintained.

RESULTS: A total of 29 NWRI studies in three Branches were supported with 14 PY's from Technical Services. This was 2 PY's less than last year. Support adjustments were made and study leaders were allowed an equitable share, and support to their priority work was provided. The lab maintenance program was completed as resources would allow. Replacement parts were obtained for several lab facilities and we conducted both routine and special maintenance on our systems. However, the tow carriage maintenance work is behind due to insufficient funding for two major tasks.

We had three high school student co-op placements and one university co-op student work in the Hydraulics and Sedimentology Laboratories. These placements were mutually beneficial.

The Sedimentology Lab staff operated and maintained the large common-user freeze dryer and conducted size analysis on sediments for many clients at CCIW as well as outside clients on a partial cost recovery basis. There is a growing interest by outside agencies to obtain size analysis and sediment dating on a cost recovery basis.

STUDY NO.: **84038**

TITLE OF STUDY: **Applied Research and Engineering**

STUDY LEADER & TEAM: **W.B. Taylor, P. Engel, J. Marsalek (RRB) and Technical Services Staff**

INTRODUCTION: This is the umbrella study for all third party revenue jobs in the Hydraulic Studies Project. In addition, administration and technical support is provided to third party revenue jobs in the Hydraulics Laboratory led by Study Leaders in the Rivers Research Branch.

RESULTS: At the beginning of this fiscal year we were projecting a revenue of at least $120K. As a result of very few large requests for services, this projection was not met. On September 1, we adjusted our target. The actual funds generated this fiscal year were $75.K There were 40 outside clients, however most jobs were small netting $200.00-$1,000.00. Only 2 jobs over $10.K were completed.